

Nonenzymatic Browning in Edible Spray-Dried Whey. Identification of Some Volatile Components

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Abstract

A steam volatile oil from commercial edible spray-dried whey, amounting to 32 mg/kg of the starting powder, has been analyzed by gas-liquid chromatography and mass spectrometry. Identities of 24 compounds were confirmed by comparison of their mass spectral and gas chromatographic data with those of authentic samples. Products identified comprise seven alkylpyrazines, three furans, two pyrroles, α -methyl- γ -butyrolactone, isobutyramide, *N*-methyl-2-pyrrolidinone, 3-hydroxy-2-butanone, benzaldehyde, phenol, benzyl alcohol, maltol, dimethylsulfone, propionic, butyric and benzoic acids. The Maillard reaction proceeded significantly during manufacture and storage. Conditions in commercial processing favor the formation of alkylpyrazines which, if taken together, are among the major volatile components of spray-dried whey.

Introduction

Whey is becoming increasingly important as a food ingredient in many products. It is estimated that 30 to 40% of the whey now being sold goes into food, and a substantial portion is used as whey powder for baked products, candies, baby foods, cereals, etc. In the first part of our work on whey (4) we studied the formation of volatile compounds in freeze-dried whey powder subjected to accelerated browning conditions. The present work was performed to determine the extent, if any, and the direction of the Maillard reaction in whey powder during commercial processing and storage.

Experimental Procedures¹

Commercial spray-dried whey. Edible spray-dried sweet whey (Extra grade) manufactured by Kraft Foods (Kraftco Corporation), Chi-

cago, Illinois, and stored for three years at 4 C was used. This product (2,790 g total) in batches of 558 g, was suspended in about one liter of dichloromethane and treated dropwise with 10% of its weight of distilled water with vigorous mechanical stirring for 30 min. The slurry was then poured into a Soxhlet thimble, and continuously extracted with dichloromethane for 20 hr. The combined extracts were evaporated at atmospheric pressure through a 33-cm helices-packed column to 100 ml, then with an aspirator to 35 ml. The residue, which consists essentially of milk fat and gels on chilling, was treated with 130 ml of water and steam distilled for 90 min to separate volatiles from the fat. The apparatus was similar to that described by Forss et al. (5), except that a spray trap was used in place of the Davies condenser. The bath was kept constant at 50 C and the pressure at 13 mm, except during the last three minutes when it was dropped to 3 mm. The steam distillate (110 ml) was saturated with sodium chloride and extracted seven times with dichloromethane (total 180 ml). The oil obtained after solvent evaporation, hereafter referred to as "spray-dried whey extract," weighed 90 mg (about 32 ppm of the original powder), and was analyzed.

Gas-liquid chromatography and mass spectrometry: analysis of spray-dried whey extract. Chromatographic and MS determinations were performed with the same columns, conditions, and the same instruments as described previously (4), but without the high-phase Column B.

The analytical procedure was similar to that used for the heated whey extract (4): the oil was fractionated with Column A (4) into seven cuts which were chromatographed on Column C (4) and the effluent analyzed by fast-scan mass spectrometry.

Reference compounds. Authentic materials previously found either in a lactose-casein model system or in whey powder subjected to accelerated browning (Table 1) were obtained or synthesized as reported earlier (2, 3, 4). A sample of 2-methyl-5-vinylpyrazine was supplied by Dr. Victor Krampl of the Corporate Research Department of the Coca-Cola Company, Atlanta, Georgia. α -Methyl- γ -butyrolactone, iso-

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¹ Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

TABLE 1. Compounds identified in the steam distillate of edible spray-dried whey.

2-Methylpyrazine ^a	2-Formylpyrrole ^a
2,5- or 2,6-Dimethylpyrazine ^{a,b}	N-Methyl-2-formylpyrrole ^{a,c}
2,3-Dimethylpyrazine ^a	α -Methyl- γ -butyrolactone
2,3,5-Trimethylpyrazine ^a	Isobutyramide
2-Methyl-5-ethyl- or 2-methyl-6-ethylpyrazine ^{a,b}	N-Methyl-2-pyrrolidinone ^{a,c}
C ₄ -Alkylpyrazine ^{a,b}	3-Hydroxy-2-butanone ^{a,c}
2-Methyl-5-vinyl- or 2-methyl-6-vinylpyrazine ^b	Benzaldehyde ^{a,c}
2-Acetylfuran ^{a,c}	Phenol ^{a,c}
Furfuryl alcohol ^{a,c}	Benzyl alcohol ^a
2-Propionylfuran ^{a,c}	Maltol ^{a,c}
	Dimethylsulfone ^c
	Propionic acid ^{a,c}
	Butyric acid
	Benzoic acid

^a Compound identified also in a lactose-casein model system (References 2, 3).

^b The isomers are indistinguishable by mass spectrometry.

^c Compound also found in whey powder subjected to accelerated browning (Reference 4).

butyramide, butyric acid, and benzoic acid were from commercial sources. All reference materials were purified by GLC.

Mass spectra. The relative intensities (in parentheses) of the eight most intense peaks (m/e) for the compounds identified in edible spray-dried whey but which were found neither in the lactose-casein (2, 3) nor in the heated whey (4) systems are presented. M⁺ designates the molecular ion.

2-Methyl-5-vinyl- or 2-methyl-6-vinylpyrazine: 120M⁺(100), 52(75), 39(47), 54(30), 119(24), 40(23), 51(23), 94(15).

α -Methyl- γ -butyrolactone: 41(100), 56(64), 42(42), 28(28), 27(28), 39(22), 29(13), 55(13).

Isobutyramide: 44(100), 43(57), 72(40), 41(37), 87M⁺(23), 27(22), 59(21), 39(16).

Butyric acid: 60(100), 73(31), 27(24), 41(21), 42(21), 88M⁺(20), 43(18), 45(16).

Benzoic acid was identified by infrared spectrum and GLC retention time.

Results and Discussion

A summary of the compounds identified in the steam distillate of commercial spray-dried whey is in Table 1. The usual criterion of positive identification was used (4). Undoubtedly the Maillard reaction proceeded to a measurable extent during manufacture and storage.

Although other alkylpyrazines have been found in milk-related systems in our laboratory (2, 3), 2-methyl-5-vinyl- or 2-methyl-6-vinylpyrazine is another addition. Benzoic acid has been identified in sterilized concentrated milk (9), and is from carbohydrate degradation (10).

Aside from dimethylsulfone, which accounts for at least 50% of the steam distillate, the most abundant components are propionic acid, butyric acid, and the alkylpyrazines (as a group).

Many compounds which have been detected in heated whey powder (4) have also been found in edible spray-dried whey. However, comparative evaluation of the results obtained with the two systems by simple comparison of the data of Table 1 with those of the preceding paper (4) is limited. The fractionating procedure for the heated whey powder extract involved a high vacuum distillation (4), whereas for commercial spray-dried whey, a steam distillation was used. The question arises, were the volatile constituents found in heated whey but apparently missing in spray-dried whey, lost during steam distillation or subsequent CH₂Cl₂ extraction from water, or were they present in amounts too small to be detected? A partial answer has been sought by a control experiment. Three microliters or 2.8 mg of all the compounds identified in heated whey but not in spray-dried whey (4) were dissolved in a small amount of dichloromethane, added to 25 ml of freshly prepared 95% milk fat, and steam distilled with 100 ml of water, using the same conditions and equipment described for the spray-dried whey extract. (2-Methyl-5-furfuryl 2'-furfuryl ether and β -acetyl- γ -butyrolactone were not included in this experiment.) The steam distillate was saturated with NaCl and exhaustively extracted with CH₂Cl₂. The residue after careful evaporation of the solvent was analyzed by GLC and MS the same as the natural mixture of unknowns. All but 13 of the 42 constituents of the synthetic mix-

ture were positively detected. Considering that the study of spray-dried whey was with about 2,800 g of powder, one can safely deduct, from our results, that the volatile components found in heated whey but missing in the spray-dried product were either present at much less than 1 ppm or were altogether absent. No conclusion can be drawn for the 13 constituents of the synthetic mixture not recovered in the control experiment. They are: difurfuryl ether, furfuryl butyrate, 2-furyl hydroxymethyl ketone, 5-(2'-furfuryl)-2-furaldehyde, 5-(5'-methyl-2'-furfuryl)-2-furaldehyde, 5-hydroxymethyl-2-furaldehyde, 2-[2'-furfuryl]-5-[2''-furfuryl] furan, β -hydroxy- γ -butyrolactone, 4,5-dihydroxyvaleric acid- γ -lactone, acetamide, glutarimide, acetol and octanoic acid.

The alkylpyrazines are, if taken together, among the major components of the steam distillate of edible spray-dried whey. Even though the available evidence is not conclusive, one can probably speculate that processing conditions are more conducive to formation of pyrazines in spray-dried whey than those of accelerated browning used in our laboratory (4). One of the current theories of pyrazine formation (1, 8) emphasizes the importance of the Streecker degradation. Possibly the processing conditions favor this pathway of the Maillard reaction (6) that leads, inter alia, to the formation of pyrazines.

Dimethylsulfide is a constituent of fresh milk. Keenan and Lindsay (7) related increased dimethylsulfide on heating to a heat labile precursor which was identified as an S-methylmethionine sulfonium salt conceivably introduced via feed from plant materials. A

possible metabolic fate of dimethylsulfide is oxidation to dimethylsulfone which accounts for the largest portion of the steam distillate of spray-dried whey.

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